

NEW POLYMERS BASED ON CELLULOSE

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Novel regioselectively functionalized cellulose derivatives were synthesized using protective group technique and selective oxidation of primary hydroxyl groups. Carboxymethyl cellulose, methyl cellulose and cellulose sulfate with a functionalization at *O*-2 and 3 were prepared via 6-*O*-(4-monomethoxy) triphenylmethyl and 6-*O*-thexyldimethylsilyl cellulose, respectively. The subsequent oxidation was

carried out with NaBr/NaClO mediated with TEMPO. The molecular structure of the new polymers was revealed by means of NMR spectroscopy.

Keywords: regioselective functionalization, 2,3-*O*-substituted cellulose, selective oxidation, 6-carboxycellulose derivatives, NMR

Introduction

Chemical modification reactions continue to provide a dominant route towards cellulose utilization in polymer-based materials. Especially products with a controlled, pre-set functionalization pattern should possess new and useful properties [1,2]. They are important in basic investigations to study for instance structure and interactions in solution and the formation of well-defined supramolecular assemblies. Moreover, studying regioselective functionalization will result in a better knowledge about reaction mechanisms and the control of processing and end-use properties. However, the synthesis of cellulose derivatives of structural uniformity is still a problem. In the course of our studies on polysaccharides, an important goal of a basic research program is the evolution of synthesis pathways due to their potential of regioselectivity. This includes of course the development of appropriate analytical tools.

In the present paper we report about the preparation of new ionic cellulose polymers obtained by using a protecting group technique as well as a selective oxidation procedure.

Materials and Methods

Cellulose powder (AVICEL PH 101, DP_{Cuoxam} 280) and spruce sulfite pulp (DP_{Cuoxam} 650, FLUKA) was used. 6-*O*-(4-monomethoxy) triphenylmethyl ("trityl") cellulose was synthesized under homogeneous reaction conditions in *N,N*-dimethylacetamide (DMA)/LiCl according to ref. [3]. The DS_{Trityl} values were determined by elemental analysis (see Table 1). The carboxymethylation of 6-mono-*O*-(4-monomethoxy)trityl cellulose and subsequent detritylation according to ref. [7] gives 2,3-*O*-carboxymethyl cellulose of a DS_{CMC} of 1.20. The 6-mono-*O*-thexyldimethylsilyl cellulose of a DS_{Silyl} of 1.04 was prepared in ammonia-saturated *N*-methylpyrrolidone. Subsequent methylation and desilylation was carried out as described in ref. [9,10] yielding 2,3-*O*-methyl cellulose (DS_{Methyl} 1.80).

Sulfation of 6-mono-*O*-(4-monomethoxy) triphenylmethyl "trityl" cellulose. In a typical example, 6 g (14 mmol) of 6-mono-*O*-(4-monomethoxy)trityl cellulose (DS_{Trityl} = 0.98) was dissolved in 150 ml dimethyl sulfoxide (DMSO). 8.9 g (56 mmol, 2 mol/mol unmodified hydroxyl group) of SO₃/pyridine complex was added at room temperature and stirring was continued for 4.5 h at room temperature. The polymer was

precipitated in 500 ml of methanol and neutralized with ethanolic sodium hydroxide solution. The product was washed with ethanol and dried in vacuum at 50°C. The product is soluble in DMSO and in water acetone mixtures (v/v = 9/1). FTIR (KBr): 1251 cm^{-1} ($\nu \text{ SO}_2$) and the characteristic signals of the triphenylmethyl moiety.

Cellulose-2,3-sulfate. 2 g of 6-mono-*O*-(4-monomethoxy)trityl cellulose-2,3-sulfate was suspended in 250 ml of methanol and 12 ml of concentrated HCl was added. The mixture was stirred for 16 h at room temperature and filtrated. The product was suspended in water and neutralized with aqueous NaOH yielding a solution. After precipitation into ethanol, the product was dried in vacuum (0.1 Torr) at 50°C. ^{13}C NMR (D_2O): δ 60.2 (C-6), 73.0-75.3 (C-2, 3, 5), 78.1-79.2 (C-4 and C-4'), 80.2 (C-2'), 82.3 (C-3'), 100.3 (C-1), 102.4 (C-1'), see Figure 2. Conditions and results of a variety of sulfating reactions of 6-*O*-(4-monomethoxy)trityl cellulose carried out according to this procedure are summarized in Table 1.

Oxidation of primary hydroxyl groups of cellulose derivatives, typical example. 1.0 g (5.3 mmol) of 2,3-*O*-methyl cellulose (DS=1.80), 7.5 mg (0.045 mmol) of 2,2,6,6-tetramethyl-1-piperidinyloxy radical (TEMPO) and 50 mg (0.48 mmol) of NaBr were dissolved in 50 ml of distilled water with stirring. A solution with a pH value of 5.0 results. The mixture was kept in an ice bath at about 1°C, and aqueous sodium hypochlorite solution (13%, w/v) was added dropwise until a pH of 10.8 was obtained. The pH value of the system was monitored. When the pH dropped below 10.8, sodium hypochlorite was added. After complete consumption of 11.0 ml of sodium hypochlorite solution the clear system obtained was precipitated in ethanol, filtered, washed with ethanol/water (v/v = 8/2) and dried in vacuum at 50°C. FTIR (KBr): 3387 ($\nu \text{ OH}$), 2891 ($\nu \text{ CH}$), 1607 and 1406 ($\nu \text{ COONa}$) 1034 ($\nu \text{ COC}$) cm^{-1} . ^{13}C NMR (D_2O): δ 58.6, 60.1 (CH_3 and C-6), 73.4-76.8 (C-2, 3 and 5), 82.4-82.8 (C-4, C-4'), 101.8 (C-1'), 174.5 (COONa).

Reaction conditions and results of oxidation reactions of regioselectively functionalized cellulose derivatives carried out according to this procedure are summarized in Table 2.

Measurements. ^{13}C NMR spectra were acquired on a Bruker DRX 400 spectrometer in DMSO-d_6 or D_2O at 25°C. The number of scans was around 6000. FTIR spectra were recorded on a Nicolet Impact 400 spectrometer using KBr pellets. The sodium content was analyzed with a flame photometer, type Flapho 41.

Results and discussion

The synthesis paths studied in this work is depicted in Figure 1. In order to selectively modify the primary hydroxyl groups of cellulose, two different protecting groups were used. On one hand, tritylation, a well-known and common method of 6-*O* protection of polysaccharides [3-7], was carried out under homogeneous reaction condition in *N,N*-dimethylacetamide (DMA)/LiCl using 4-monomethoxytriphenylchloromethane [3]. By this effective procedure a 6-*O*-(4-monomethoxy)triphenylmethyl ("trityl") cellulose (1-3) of high regioselectivity was obtained. On the other hand, the possibility to protect polysaccharides with bulky trialkylsilyl moieties was studied recently in detail [8-10]. The silylation of cellulose with hexyldimethylchloro-silane under heterogeneous reaction conditions in ammonia-saturated *N*-methylpyrrolidone at -15°C yields 6-*O*-hexyldimethylsilylcellulose (4) with a DS_{silyl} of 1.04 and a complete reaction at *O*-6.

Synthesis of 2,3-*O*-functionalized products via 6-*O*-(4-monomethoxy)trityl cellulose. Due to the stability of 4-monomethoxytrityl groups under alkaline conditions we were able to prepare 2,3-*O*-carboxymethyl cellulose. The 6-*O*-(4-monomethoxy)trityl cellulose was dissolved in dimethyl sulfoxide (DMSO) and activated by solid NaOH powder.

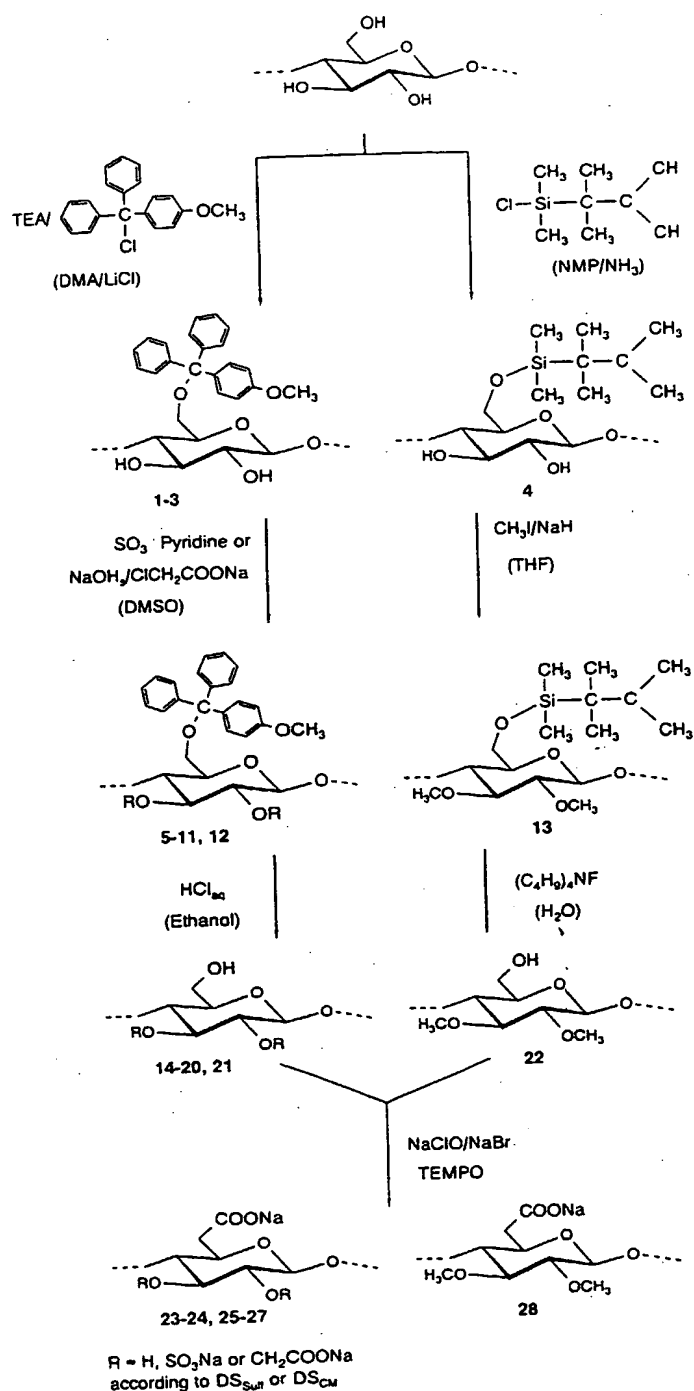


Figure 1. Synthesis paths for regioselective functionalization of cellulose.

The conversion with monochloroacetate and subsequent detritylation with HCl afforded the 2,3-O-CMC (12, 21) as described in detail in ref. [7, 11]. However, no information about sulfation of 6-O-(4-monomethoxy)trityl cellulose were available up to now.

The sulfation of the 6-O protected samples 1-3 was carried out homogeneously in DMSO using SO_3 -pyridine complex as sulfating agent at room

temperature (Tab. 1). After a reaction time of 2 to 4.5 h, the products were precipitated in methanol and neutralized with ethanolic NaOH solution in order to transfer the free acid form of the sulfuric acid half esters into the sodium salt form. This is very important to prevent an acid degradation of the polymer chain as well as an undesired acidic detritylation. The products obtained are very hygroscopic yielding rubber like materials by attracting water. The 6-O-(4-monomethoxy)trityl cellulose sulfates (sodium salt) are soluble in DMSO and mixtures of water/acetone (v/v = 9/1). They possess surface active properties.

The FTIR spectra of these polymers 5-11 show the characteristic absorptions of the sulfuric acid half esters. Peaks are visible at 1251 cm^{-1} (νSO_2) and 810 cm^{-1} (νSO), however the last one is mixed with the signal of the C-H vibration of the aromatics (δCH). The typical peaks of the trityl moieties at 3028 and 1608 cm^{-1} (νCH and CC) are also found in the spectra.

By exposing the 6-O-(4-monomethoxy)trityl cellulose-2,3-sulfate to controlled acidic conditions the trityl group can be complete removed yielding a pure cellulose-2,3-sulfate. In the FTIR spectra of the detritylated products the signals in the aromatic region disappear. The $\text{DS}_{\text{Sulfate}}$ values were determined by means of elemental analysis. It was found that during the detritylation a partial removal of sulfuric acid half ester groups occurs as well (Tab. 1).

The ^{13}C NMR spectra of the cellulose sulfates recorded in D_2O show the characteristic signals of the carbon atoms of the modified AGU in the range between 60.2 and 102.6 ppm. From the spectra it may be concluded that no sulfation of the primary hydroxyl groups took place if the $\text{DS}_{\text{Trityl}}$ is 0.98 (samples 8-11). There is a peak for the C-6 bearing a OH group at $\delta = 60.2$ ppm only. On the other hand, the peaks at $\delta = 80.5$ (C-2_s) and 81.3 (C-3_s) indicate the exclusive reaction at these positions (Figure 2).

Synthesis of regioselectively functionalized products via 6-mono-O-thexyldimethylsilyl cellulose. Due to their high regioselectivity, the bulky trialkylsilyl cellulose represents valuable and versatile reactive intermediates for subsequent regioselective reactions. The silyl function can be used as an activating group as

well as an protecting group. For example, the reaction with SO_3 proceeds via insertion of SO_3 into the Si-O bond. Consequently, this polymer is not suitable for the preparation of cellulose-2,3-sulfates. However, methylation of 6-*O*-thexyldimethylsilyl cellulose with methyl iodide

in the presence of NaH occurred at the free OH-groups only (13). Treatment with tetrabutylammonium fluoride to remove the thexyldimethylsilyl afforded pure 2,3-di-*O*-methyl cellulose (22).

Table 1. Results of the sulfation of 6-*O*-(4-monomethoxy)trityl cellulose (MMTC) with 2 mol sulfating agent per mol unmodified hydroxyl group (in dimethyl sulfoxide at room temperature).

MMTC		Reaction conditions		MMTC sulfate			Cellulose sulfate		
No.	DS _{Trityl} ^a	Sulfating agent	Time (h)	No.	S (%)	DS _{Sulfate} ^a	No.	S (%)	DS _{Sulfate} ^a
1	0.60	SO ₃ -DMF	2.5	5	7.55	0.93	14	5.37	0.32
2	0.83	SO ₃ -Py	2.0	6	-	-	15	5.91	0.37
2	0.83	SO ₃ -Py	2.5	7	-	-	16	6.75	0.44
3	0.98	SO ₃ -Py	2.0	8	-	-	17	4.92	0.30
3	0.98	SO ₃ -DMF	2.5	9	9.30	1.80	18	8.22	0.57
3	0.98	SO ₃ -Py	2.5	10	-	-	19	9.59	0.70
3	0.98	SO ₃ -Py	4.5	11	-	-	20	12.00	0.99

a) DS, Degree of substitution calculated on basis of elemental analysis

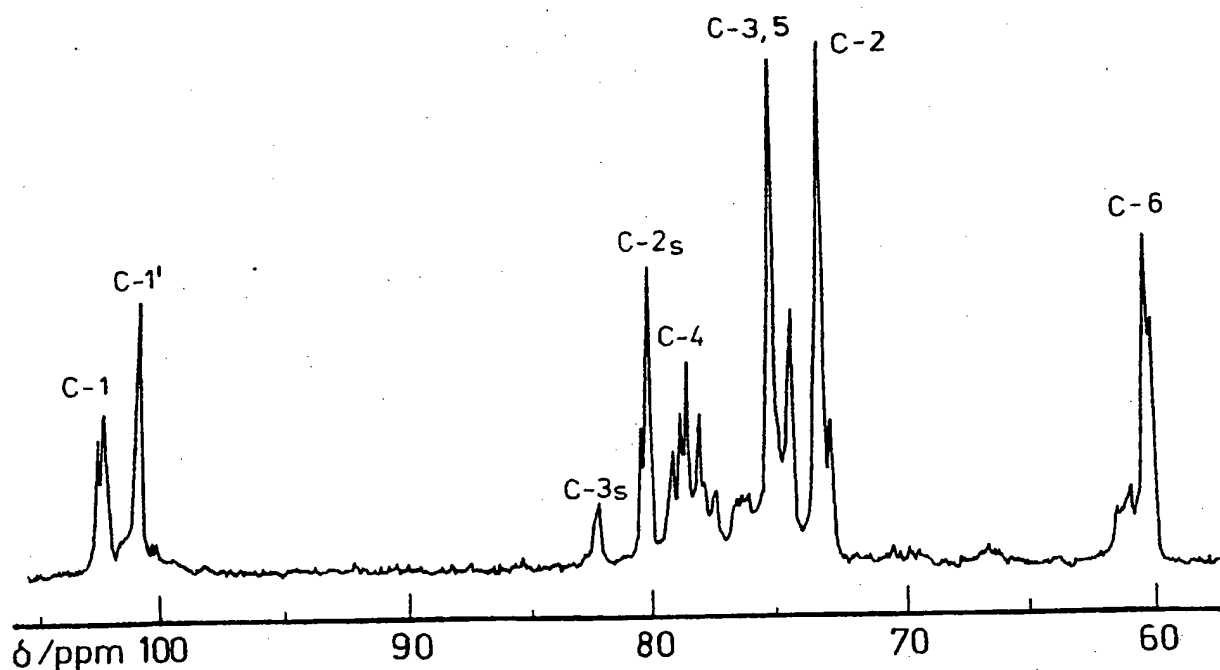


Figure 2. ^{13}C -NMR spectrum of cellulose-2,3-sulfate 20.

Oxidation of 2,3-O-functionalized cellulose derivatives. Recently, de Nooy *et al.* succeeded in the selective oxidation of water-soluble polysaccharides like starch, inulin, and pullulan [12, 13]. The oxidation is carried out in water homogeneously and is mediated by 2,2,6,6-

tetramethyl-1-piperidinyloxy radical (TEMPO) using hypobromite as the oxidizing agent and NaOH to control the pH value of the reaction medium. The oxidation method was applied to cellulose as well [14]. The cellulose has to be strongly activated by mercerization prior to

oxidation. In our own work, the oxidation of water-soluble hydroxyethyl cellulose was investigated. It was found that the adjustment of the pH-value is very important for both a selective oxidation and low chain degradation [15]. It is worth mentioning that the pH-value can be adjusted by the oxidation agent NaClO itself, *i.e.*, the additional use of aqueous NaOH is not necessary.

Table 2. Conditions and results of the oxidation of cellulose derivatives.

Starting polymer			Molar ratio ^b	Rxn. time (min)	Oxidized polymer	
No.	Type ^a	DS ^a			No.	DO ^c
21	CMC	1.2	5	10	23	0.8
21	CMC	1.2	5	30	24	1.0
13	CS	0.3	5	25	25	0.9
15	CS	0.4 ^d	5	20	26	0.8
18	CS	0.7	5	10	27	0.5
22	MC	1.8	10	40	28	1.0

a) MC, 2,3-*O*-methyl cellulose; CMC, 2,3-*O*-carboxymethyl cellulose; CS, cellulose-2,3-sulfate; DS, degree of substitution

b) NaClO / AGU (Anhydroglucose unit) [mol/mol]

c) Degree of oxidation (DO) calculated from sodium content determined by means of flame photometry

d) Partially functionalized at the 6 position (DS 0.2)

For the oxidation of regioselectively 2,3-functionalized cellulose derivatives (see Fig. 1), the polymers 15, 18, 21, and 22 were dissolved in water containing a catalytic amount of TEMPO and NaBr. Aqueous sodium hypochlorite solution was added maintaining a constant pH value of 10.8 (Tab. 2.). The ¹³C-NMR spectra of the isolated products show, compared to the starting polymers, new peaks at about $\delta = 175$ ppm indicating the transformation of the CH₂OH to a COONa group (Figure 3).

The aqueous solution of the oxidized polymers show lower viscosity values compared to the starting materials. This might be a consequence of the introduction of carboxyl groups and probably a result of depolymerization as a side reaction. Preliminary GPC measurements show that only a low chain degradation occurs under the oxidation conditions applied. However, additional studies have to be carried out due to the known problems of the determination of the molecular mass of cellulose derivatives by means of GPC.

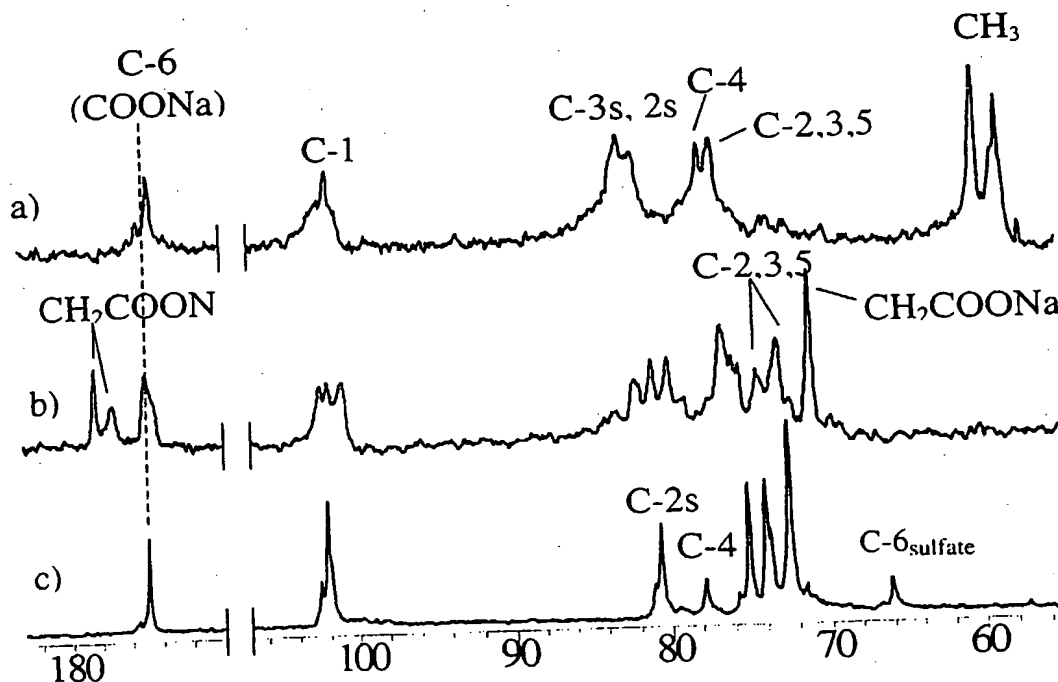


Figure 3. ¹³C-NMR spectra of a) 6-carboxy-2,3-*O*-methyl cellulose with degree of oxidation (DO) = 1.0 and degree of substitution (DS) = 1.8, b) 6-carboxy-2,3-*O*-carboxymethyl cellulose, DO = 1.0, DS = 1.2 and c) 6-carboxy-cellulose sulfate, DO = 0.8 and DS = 0.4 (partially sulfated at position 6)

Conclusions

The synthesis paths studied represent interesting routes to new polymers based on cellulose. The products obtained by a protecting group technique and a selective oxidation possess a very uniform distribution of the functional groups. The molecular structure was evaluated in detail by means of ^{13}C -NMR spectroscopy. The properties of the new polymers (behavior in solution, interaction with cations, gel and simplex formation) are under investigation.

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